

PATENT ABSTRACTS OF JAPAN

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(54) ELECTRO CONDUCTIVE THERMOPLASTIC ELASTOMER COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a recyclable thermoplastic elastomer composition where an electrical conductivity is imparted and workability is good.

SOLUTION: An electro conductive thermoplastic elastomer composition is formed by dispersing a carbon nanotube to a thermoplastic elastomer material where a rubber is blended to a thermoplastic elastomer, and (a) a rubber portion of the thermoplastic elastomer material is crosslinked by a resin crosslinking agent to have compression set of 30% or less, (b) a blended amount of the rubber is in a ratio of 225 to 400 parts by weight based on the 100 parts by weight of the thermoplastic elastomer and (c) the carbon nanotube has a diameter of 70 nm or less. The composition has a smooth side surface formed with the shape where graphen sheets are rounded and is such a composition that a plurality of layers composed of graphen sheets are arranged in a concentrically circular state.

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CLAIMS

[Claim(s)]

15 [Claim 1] Into the thermoplastic-elastomer ingredient which blended rubber with thermoplastic elastomer It is the conductive thermoplastic-elastomer constituent which is made to distribute a carbon nanotube and changes. (a) The bridge is constructed over a part for the rubber of said thermoplastic-elastomer ingredient by the resin system cross-linking agent. A compression set (K JIS 6262 law and 70 degrees C 22 hours after) is 30% or less. (b) The loadings of said rubber are the rate of the 225 - 400 weight section to said thermoplastic-elastomer 100-weight section. The (c) aforementioned carbon nanotube The conductive thermoplastic-elastomer constituent characterized by what a diameter is 70nm or less and the layer which has the smooth side face which consists of a configuration where the graphene sheet was rounded off, and consists of a graphene sheet is what is arranged two or more concentric circular.

20 [Claim 2] The conductive thermoplastic-elastomer constituent according to claim 1 characterized by making the thermoplastic-elastomer ingredient which comes to carry out dynamic bridge formation of the rubber by the resin system cross linking agent distribute a carbon nanotube later, and growing into it, kneading thermoplastic elastomer and rubber.

25 [Claim 3] The conductive thermoplastic-elastomer constituent according to claim 2 characterized by performing said dynamic bridge formation using an extruder.

30 [Claim 4] The conductive thermoplastic-elastomer constituent according to claim 1 characterized by making said thermoplastic-elastomer ingredient distribute the carbon nanotube which thermoplastics was made to distribute beforehand.

35 [Claim 5] The conductive thermoplastic-elastomer constituent according to claim 1 to 4 characterized by making it come to thermoplastic elastomer and the total quantity 100 weight section of rubber to distribute a carbon nanotube 1 - 30 weight section.

40 [Claim 6] The conductive thermoplastic-elastomer constituent according to claim 1 to 5 characterized by for said thermoplastic elastomer being styrene-ethylene-butylene-styrene resin, styrene-ethylene-propylene-styrene resin, or styrene-ethylene-ethylene-propylene-styrene resin, and said rubber being ethylene-propylene rubber (EPM) or ethylene-propylene-diene rubber (EPDM).

[Claim 7] The conductive thermoplastic-elastomer constituent according to claim 1 to 6 characterized by a compression set (K JIS 6262 law and 70 degrees C 22 hours after) being 30%

or less.

DETAILED DESCRIPTION

5 [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention has the outstanding mechanical property (it is a low compression set and has flexibility), and relates to a recyclable conductive thermoplastic-elastomer constituent.

10 [0002]

[Description of the Prior Art] Generally, in order to give conductivity to a giant-molecule constituent, add conductive ingredients, such as carbon black, a metal powder, and a metal fiber, the polymeric materials itself are made into the thing of high conductivity, or the means of adding ion electric conduction agents, such as an electrolyte, are taken. The means which makes the polymeric materials itself high conductivity in this has the problem that cost becomes high, and it becomes hard, and an elastomer-like thing is hard to be obtained. Moreover, since it is necessary to add it so much in order to give conductivity although a means to add a conductive ingredient which was described above is low cost comparatively, when workability is dramatically inferior and the front face of a giant-molecule product is moreover worn, carbon black etc. occurs in the shape of dust, and a possibility of soiling a pure ambient atmosphere also has it. A means to add an electrolyte etc. is difficult to carry out bleeding to a front face from the field of compatibility with polymeric materials, and to give conductivity more than a certain fixed level.

20 [0003] In recent years, utilization of a carbon nanotube (or super-thin carbon fibril) is advanced, and it is added for the object, such as a reinforcing agent and an electro-conductivity applying agent, also to polymeric materials (the patent No. 2863192 official report, the patent No. 2588626 official report, the patent No. 3034027 official report, JP, 8-27279,A, and JP, 2000-357419,A).

30 [0004] In this, the super-thin carbon fibril 1 - 50 weight *****, and the thermoplastic-elastomer constituent over which the bridge was constructed are indicated by the patent No. 2863192 official report per total quantity 100 weight section of thermoplastic elastomer (100 weight sections) and a rubber-like polymer (0 - 200 weight section). Here, if a rubber-like polymer is used more than the 200 weight sections to the thermoplastic-elastomer 100 weight section, although the reinforcement effectiveness based on the outstanding compatibility of thermoplastic elastomer and super-thin carbon fibril is no longer discovered, no example which blended the rubber-like polymer actually is shown.

35 [0005]

40 [Problem(s) to be Solved by the Invention] When stress is applied to an ingredient, thermoplastic elastomer can repeat the cycle which will be in the condition that there is reinforcement comparatively firmly, if an ingredient becomes soft and flows and cools with a temperature rise. Although adding a carbon nanotube to thermoplastic elastomer and giving conductivity to it is known as aforementioned, the thermoplasticity of the

thermoplastic-elastomer constituent obtained is maintained, and it is hard to say the improvement in a mechanical property (for example, for a compression set to be made low) that drawing is. For example, in the aforementioned patent No. 2863192 official report, the thermoplastic-elastomer constituent obtained actually is only what carried out press cure of the thermoplastic-elastomer independent system, using a sulfur system cross linking agent as polymeric materials. In view of that manufacture condition, thermoplasticity has disappeared and the recycle activity of this last constituent cannot be carried out easily as it is.

[0006] Then, the object of this invention adds a carbon nanotube to thermoplastic elastomer, gives conductivity, it has recycle nature, without moreover losing thermoplasticity, and tends to offer the conductive thermoplastic-elastomer constituent which has mechanical properties, such as a compression set, and was excellent in workability.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, when this invention persons advance examination wholeheartedly, they succeed in obtaining the conductive thermoplastic elastomer of the expected object also unexpectedly by blending a lot of rubber, constructing the bridge over the rubber, and distributing a carbon nanotube into the thermoplastic-elastomer ingredient whose compression set is 30% or less rather than having become known to thermoplastic elastomer conventionally.

[0008] That is, it is the conductive thermoplastic-elastomer constituent which the thermoplastic-elastomer ingredient which blended rubber with thermoplastic elastomer is made to distribute a carbon nanotube, and grows into it, the bridge is constructed over a part for the rubber of the (a) aforementioned thermoplastic-elastomer ingredient by the resin system cross linking agent, and the conductive thermoplastic elastomer of this invention is a compression set (the measured value of 22 hours after is said at 70 degrees C by K JIS 6262 law.). the following — being the same — 30% or less — it is — (b) — the loadings of said rubber — said thermoplastic-elastomer 100 weight section — receiving — the 225 - 400 weight section — comparatively — coming out — it is — (c) — said carbon nanotube is characterized by what a diameter is 70nm or less and the layer which has the smooth field which consists of a configuration where the graphene sheet was rounded off, and consists of a graphene sheet is what is arranged two or more concentric circular.

[0009] The conductive thermoplastic-elastomer constituent of this invention can be used with profitability sufficient as an electrical conducting material of various kinds of electrical parts or electronic parts from excelling in mechanical properties, such as a compression set, and moreover having recycle nature.

[0010] The conductive thermoplastic-elastomer constituent of this invention includes the following embodiment. In the conductive thermoplastic-elastomer constituent of aforementioned this invention, after kneading thermoplastic elastomer and rubber, it is characterized by making the thermoplastic-elastomer ingredient which comes to carry out dynamic bridge formation of the rubber distribute a carbon nanotube, and growing into it. In the conductive thermoplastic-elastomer constituent of aforementioned this invention, it is characterized by performing said dynamic bridge formation using an extruder.

[0011] In the conductive thermoplastic-elastomer constituent of aforementioned this invention, it is characterized by making said thermoplastic elastomer distribute the carbon nanotube which

thermoplastics was made to distribute beforehand. In the conductive thermoplastic-elastomer constituent of aforementioned this invention, it is characterized by making it come to thermoplastic elastomer and the total quantity 100 weight section of rubber to distribute a carbon nanotube 1 – 30 weight section.

5 [0012] In the conductive thermoplastic-elastomer constituent of aforementioned this invention, it is characterized by a compression set being 30% or less.

[0013]

10 [Embodiment of the Invention] The conductive thermoplastic-elastomer constituent of this invention adds the chemical which constructs a bridge in a part for rubber, kneading this thermoplastic-elastomer ingredient at the elevated temperature near 200 degree C including the rubber of said amount of specification blended with thermoplastic elastomer and this as indispensable polymeric materials, advances bridge formation for rubber, and is obtained by subsequently distributing a carbon nanotube.

15 [0014] Viscosity falls by having thermoplasticity, i.e., heat, and the thermoplastic elastomer set to one of the ingredients in this invention becomes soft, and when it cools, it should just be polymeric materials which become what has rubber elasticity. As thermoplastic elastomer, it is desirable to especially use styrene-ethylene-butylene-styrene resin and styrene-ethylene-propylene-styrene resin, and the styrene-ethylene-ethylene-propylene-styrene (SEEPS) resin of reinforcement which contains
20 the repeat unit of ethylene in a principal chain further is expensive, and divides from a compression set from the first being small and is desirable. As an example of SEEPS, a trade name "SEPUTON 4077", "SEPUTON 4055", and "SEPUTON 4033" (all are Kuraray Make) are mentioned. Also in these, "SEPUTON 4077" which has about 300,000 and high molecular weight divides the number average molecular weight by GPC, and it can be used preferably.

25 [0015] Which rubber is sufficient as the rubber which serves as another ingredient in this invention, for example, it is natural rubber and cis-1,4-polyisoprene, high cis-polybutadiene, styrene-butadiene copolymer rubber, ethylene-propylene rubber (EPM), ethylene-propylene diene rubber (EPDM), chloroprene rubber, isobutylene isoprene rubber, halogenation isobutylene isoprene rubber, acrylonitrile-butadiene copolymer rubber, or acrylic rubber is mentioned.

30 [0016] Also in these, from the field of compatibility with thermoplastic elastomer, if EPM or EPDM is desirable and takes cross-linking into consideration, EPDM will be used most preferably. As EPDM, various kinds of things are usable, what has a low ethylene content is excellent in low temperature-dependency-characteristics nature, and what has a high ethylene content tends to be excellent in reinforcement. Moreover, an oil exhibition type is sufficient as
35 EPDM. In this invention, although rubber is blended at a rate of the 250 – 400 weight section to the thermoplastic-elastomer 100-weight section as aforementioned, a still more desirable rate is the range of the 300 – 350 weight section. If the amount of rubber exceeds the above-mentioned range, in the bridge formation process of next rubber, it becomes difficult to maintain the thermoplasticity of thermoplastic elastomer, and when not arriving at the
40 above-mentioned range on the other hand, a compression set will get worse. In addition, although an oil exhibition type is sufficient as rubber as mentioned above, the oil to which the oil exhibition of the above-mentioned rubber weight rate was carried out is not contained.

[0017] It is not efficient to prepare with a batch type-kneading machine on the occasion of

preparation of the thermoplastic-elastomer ingredient which blended rubber with thermoplastic elastomer, and it is desirable to prepare carrying out dynamic bridge formation of the part for rubber using the extruder of continuous system. Although either of the cross linking agent of a resin system and a peroxide system is possible for bridge formation once to this dynamic bridge formation, when a bridge formation rate, an odor, physical properties, etc. are taken into consideration for bridge formation by the extruder, resin bridge formation is actually the most desirable to it. Dramatically, an odor is strong and a vulcanization degree does not go up it by sulfur bridge formation, either. It is also possible that vulcanization in an extruder cannot progress easily, and control is difficult and peroxide vulcanization causes fume also by reaction ****.

[0018] the reaction type in which alkylphenol formaldehyde resins are desirable and have especially a bromine as a resin cross linking agent — desirable — as an example — a trade name "the tacky roll 201" and "tacky roll 250-I" — or — adjustment of a degree of cross linking is possible by being able to mention tacky roll 250-III" (all being the products made from the Taoka chemistry) etc., and using, combining these suitably. a cross linking agent — the rubber 100 weight section — receiving — 5 - 20 weight section — it is the range of 10 - 15 weight section preferably. Moreover, the thing made for a zinc oxide to usually exist for a resin vulcanization — required — as the amount — the rubber 100 weight section — receiving — 1 - 10 weight section — it is the range of 2 - 5 weight section preferably.

[0019] In this invention, by in addition to an aforementioned plasticity elastomer and rubber, blending other resin ingredients, for example, blending olefine resin division polypropylene, the appearance of a conductive thermoplastic-elastomer constituent is raised, reinforcement is enlarged, and a sex with a blemish-proof is improved. A homopolymer is sufficient as polypropylene and it may be block polymer with an ethylene unit, or the random copolymer of ethylene and a propylene. As for polypropylene, it is desirable to blend at a rate of 5 - 40 weight section to the total quantity 100 weight section of thermoplastic elastomer and rubber, and its range of 10 - 20 weight section is more desirable especially.

[0020] Moreover, the thing made for the conductive thermoplastic elastomer of this invention to contain oil in order to improve improvement in flexibility, and workability — possible — as the amount — the total quantity 100 weight section of thermoplastic elastomer and rubber — receiving — the 0 - 300 weight section — desirable — the 20 - 200 weight section — it is the 50 - 150 weight section still more preferably. Furthermore, if needed, unless the object of this invention is checked for an antioxidant, light stabilizer, an ultraviolet ray absorbent, a pigment, a bulking agent, or processing aid, optimum dose may be added. Said thermoplastic-elastomer ingredient is prepared by extruding said thermoplastic elastomer and rubber near 200 degree C and on condition that screw-speed 200rpm extent etc. using a biaxial extruder with the additive blended if needed [such as a rubber cross linking agent.]. In this ingredient, if it sees microscopically, a bridge will be constructed over rubber and it will become a small island, and it is in the condition of resin, such as polypropylene blended with thermoplastic elastomer if needed, of so to speak having appeared all over the sea. Thus, since the amount of [over which the obtained thermoplastic-elastomer ingredient constructed the bridge rather than the thermoplastic-elastomer independent case] rubber exists, a compression set may become small, may become 30% or less, and may be below 20%. Moreover, injection molding and extrusion

molding are also possible.

[0021] Next, a carbon nanotube is distributed in the above-mentioned thermoplastic-elastomer ingredient. The thing of various kinds of types is known and a carbon nanotube has size also in extent of a path. Generally, what has a smaller diameter has larger surface area, and is advantageous in the field which gives conductivity. In this invention, that whose average diameter is 15-30nm is desirable, if it is 20nm or less, it is still more desirable, and if the diameter is substantially fixed, it is more desirable. Furthermore, the layer which has the smooth side face which consists of a configuration where the graphene sheet was rounded off, and consists of a graphene sheet should just be arranged two or more concentric circular. Since die length is cut by kneading, generally the range is not restricted to the range of **** using an about 100 to 1000 times [of a diameter] thing, although texture ***** is difficult. The carbon nanotube of such engine performance is already marketed, for example, can use the thing by the high virion KYATARISHISU international company.

[0022] In this invention, it is desirable to distribute 1 - 30 weight section to thermoplastic elastomer and the total quantity 100 weight section of rubber, and if a carbon nanotube is 4 - 8 weight section also in this range, it is much more desirable. If it is such addition range, conductivity can be given and the workability of the conductive thermoplastic elastomer moreover obtained will not be reduced substantially. The conductivity as used in the field of this invention means that they are below 107ohm and cm that can be measured to stability, when a volume resistivity value is measured with a resistance measuring device (for example, thing by ADVANTEST CORP.). A carbon nanotube can also blend the masterbatch which could add and distribute into the above-mentioned thermoplastic-elastomer ingredient as it was, and thermoplastic elastomer or other thermoplastics was made to distribute beforehand. Here, although especially the class of other thermoplastics is not limited, polypropylene, polystyrene, or polyethylene is desirable as an ingredient with sufficient compatibility with thermoplastic elastomer. Besides it, thermoplastics, such as a polycarbonate, a polyamide, polyester, or polyurethane, can be mentioned.

[0023] A carbon nanotube can be distributed in the above-mentioned charge of a compounding agent by kneading again said thermoplastic-elastomer ingredient and carbon nanotube (or the masterbatch), for example with a biaxial extruder, Banbury and a kneader, a small kneading machine, etc. In the point which can be manufactured continuously, the activity of a biaxial extruder is advantageous also in these types of inside. The distributed situation of a carbon nanotube — 2 times — or it may supply to a biaxial extruder repeatedly 3 times or more, more kneading may be given, and distribution may be received. Generating of static electricity uses the thermoplastic-elastomer constituent of this invention as an ingredient of various kinds of electrical parts or electronic parts as polymeric materials excellent in few mechanical properties, and it can carry out the thing of it. For example, it can be used for OA components, such as housing material of OA equipment, and a driving roller of conductive flooring and a medium imprint belt, etc.

[0024]

[Example] An example and the example of a comparison are given to below, and this invention is explained to it still more concretely.

[0025] The paraffin oil 57 weight section was added as example 1 thermoplastic elastomer in

the SEEPS (trade name "SEPUTON 4077" Kuraray Make) 32 weight section and the polypropylene 11 weight section, and it extruded and pelletized by 180 degrees C and 200rpm using every night and the biaxial 1 shaft extruder (product made from eye PEKKUSU). To this, the zinc-oxide 3.5 weight section, the resin system cross linking agent (trade name "tacky roll" mixture of 201 and 3:1 with "250-III" (product made from Taoka chemistry)) 12 weight section, as the polypropylene 15 weight section and rubber — the EPDM (trade name "S PUREN 670F", Sumitomo Chemical make) 200 weight section (the oil 100 weight section is included) — in addition, the same biaxial 1 shaft extruder was supplied, dynamic bridge formation was performed by 200 degrees C and 200rpm, and the thermoplastic-elastomer ingredient was obtained. It was 13%, when the thermoplastic-elastomer ingredient obtained above was fabricated and the compression set was measured.

[0026] Next, the masterbatch (carbon nanotube weight fraction [of 20%], carbon nanotube average diameter of 20nm; high peri ONKYATARISHISU international company make) 40 weight section of the polystyrene base of a carbon nanotube was added in this thermoplastic-elastomer ingredient 330.5 weight section, it kneaded by 200 degrees C and 200rpm with the biaxial extruder (Kobe Steel, Ltd. make) in it, and the conductive thermoplastic-elastomer constituent of this invention was obtained in it.

[0027] When the conductivity of this thermoplastic-elastomer constituent was measured with the resistance-measuring device (ADVANTEST CORP. make), the volume resistivity value was below a limit of measurement (107 ohm-cm). Since the thin strand was obtained when this conductive thermoplastic-elastomer constituent was extruded at 200 degrees C with the Monsanto processor BIRITI circuit tester, it has checked that it was thermoplasticity. Moreover, when this conductive thermoplastic-elastomer constituent is fabricated and a compression set is measured, it is 25%, and the value which was fully excellent was shown. Furthermore, when this conductive thermoplastic-elastomer constituent was extruded in the shape of a tube with the extruder of one shaft, the tube of a very beautiful appearance was obtained.

[0028] Except having made the masterbatch of the polystyrene base of a carbon nanotube into 20 weight sections in example 2 example 1, it prepared like the example 1 and the conductive thermoplastic elastomer of this invention was obtained. Moreover, when volume resistivity was measured, they were 1011 ohm-cm.

[0029] The paraffin oil 57 weight section was added as example 3 thermoplastic elastomer in the SEEPS (trade name "SEPUTO 4077" Kuraray Make) 32 weight section and the polypropylene 11 weight section, and it extruded and pelletized by 180 degrees C and 200rpm using every night and the biaxial 1 shaft extruder (product made from eye PEKKUSU). this — as the zinc-oxide 3.5 weight section, the resin system cross linking agent 9 weight section, the polypropylene 15 weight section, and rubber — the EPDM(trade name "S PUREN 670F", Sumitomo Chemical make) 144 weight section (the oil 72 weight section is included) — in addition, the same biaxial 1 shaft extruder was supplied, dynamic bridge formation was performed by 200 degrees C and 200rpm, and the thermoplastic-elastomer ingredient was obtained.

[0030] Next, the masterbatch (carbon nanotube weight fraction [of 20%], carbon nanotube average diameter of 20nm; high peri ONKYATARISHISU international company make) 40 weight section of the polystyrene base of a carbon nanotube was added in this

thermoplastic-elastomer ingredient 271.5 weight section, it kneaded by 200 degrees C and 200rpm with the biaxial extruder (Kobe Steel, Ltd. make) in it, and the conductive thermoplastic-elastomer constituent of this invention was obtained in it. This volume resistivity was below a limit of measurement.

5 [0031] Thermoplastic elastomer was obtained like the example 3 except having added and carried out dynamic bridge formation of the EPDM (trade name "S PUREN 670F", Sumitomo Chemical make) 256 weight section (the oil 128 weight section being included) as the example 4 resin system cross linking agent 16 weight section and rubber. The masterbatch 40 weight section of the polystyrene base of a carbon nanotube was added in this
10 thermoplastic-elastomer ingredient 390.5 weight section, and the conductive thermoplastic-elastomer constituent was obtained like the example 3 except having kneaded with the biaxial extruder. This volume resistivity was 107 and cm.

[0032] Except having made the masterbatch of the polyethylene base of a carbon nanotube additive-free in example of comparison 1 example 1, it prepared like the example 1 and
15 thermoplastic elastomer was obtained. It was 13%, when this thing was fabricated and permanent compressive strain were measured. Moreover, when volume resistivity was measured, they were 1016 ohm-cm.

[0033] Except having made the masterbatch of the polyethylene base of a carbon nanotube into 5 weight sections in example of comparison 2 example 1, it prepared like the example 1 and
20 thermoplastic elastomer was obtained. Although it was 17% when this thing was fabricated and permanent compressive strain were measured, the volume resistivity values were 1016 ohm-cm.

[0034] To the thermoplastic elastomer prepared in example of comparison 3 example 1, it replaced with the carbon nanotube and the KETCHIEN black EC25 weight section was added using the biaxial extruder. Although the volume resistivity of this preparation object was below a
25 limit of measurement, when the compression set was measured, it was 38% and was that too high. Moreover, when the tube was slowly extruded with 1 shaft extruder, temperature went up too much and only the tube of the rough appearance was obtained.

[0035] The paraffin oil 57 weight section was added as example of comparison 4 thermoplastic elastomer in the SEEPS(trade name "SEPUTON 4077", Kuraray Co., Ltd. make) 32 weight
30 section and the polypropylene 11 weight section, and it extruded and pelletized by 180 degrees C and 200rpm using every night and the biaxial 1 shaft extruder (ice peck company make). The masterbatch (carbon nanotube weight fraction [of 20%], carbon nanotube average diameter of 20nm; high peri ONKYATARISHISU international company make) 20 weight section of the polyethylene base of a carbon nanotube was added to this, and with the biaxial extruder (Kobe
35 Steel, Ltd. make), it kneaded and fabricated by 200 degrees C and 200rpm. When the compression set of this preparation object was measured, they were 38% and a too high thing. In addition, volume resistivity was below a limit of measurement.

[0036]

[Effect of the Invention] Since what times or injection molding is possible (that is, a recycle
40 activity is possible), for example, the scrap wood within a process can also use the thermoplastic-elastomer constituent of this invention without futility, a manufacturing cost is reduced. In this invention, since the thermoplastic-elastomer ingredient prepared before distributing a carbon nanotube contains a part for the rubber over which the bridge was

constructed with thermoplastic elastomer, it has a compression set low like it does not become as compared with usual thermoplastic elastomer. That is, the compression set of the thermoplastic-elastomer constituent with which, as for the compression set, usual thermoplastic elastomer distributed the carbon nanotube of this invention to being usually 40% or more is 30% or less, and a durometer A degree of hardness is before and after 50, and since it is dramatically flexible, in using for an electrical part or electronic parts, it has a very good mechanical property.

[0037] Moreover, according to this invention, the conductive thermoplastic-elastomer constituent obtained is excellent in a fluidity, and extrusion molding and the product of an appearance very beautiful also when it injection molds are obtained from the ability of conductivity to be given even if the addition of a carbon nanotube is dramatically little as compared with the conventional addition-of-conductivity matter, for example, usual carbon black etc.

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(54) 【発明の名称】 導電性熱可塑性エラストマー組成物

(57) 【要約】

【課題】 導電性が付与されており、しかも加工性がよくリサイクル可能な熱可塑性エラストマー組成物を提供する。

【解決手段】 熱可塑性エラストマーにゴムを配合した熱可塑性エラストマー材料に、カーボンナノチューブを分散させて成る導電性熱可塑性エラストマー組成物にあって、(a) 前記熱可塑性エラストマー材料のゴム分が樹脂系架橋剤により架橋されていて圧縮永久歪みが30%以下であり、(b) 前記ゴムの配合量が前記熱可塑性エラストマー100重量部に対して225~400重量部の割合であり、(c) 前記カーボンナノチューブは、直径が70nm以下であり、グラフェンシートを丸めた形状からなる平滑な側面を有し、かつグラフェンシートからなる層が複数同心円状に配置されているものである、導電性熱可塑性エラストマー組成物。

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【0006】そこで、本発明の目的は、熱可塑性エラス

トマーにカーボンナノチューブを添加して導電性を付与し、しかも熱可塑性を失うことなくリサイクル性があり、圧縮永久歪みなどの機械的特性を有し加工性に優れた導電性熱可塑性エラストマー組成物を提供しようとするものである。

【0007】

【課題を解決するための手段】本発明者らは、上記の課題を解決するために鋭意検討を進めたところ、熱可塑性エラストマーに従来知られているよりも多量のゴムを配合し、そのゴムが架橋されており、圧縮永久歪みが30%以下である熱可塑性エラストマー材料に、カーボンナノチューブを分散することにより、意外にも所期目的の導電性熱可塑性エラストマーを得ることに成功したものである。

【0008】すなわち、本発明の導電性熱可塑性エラストマーは、熱可塑性エラストマーにゴムを配合した熱可塑性エラストマー材料に、カーボンナノチューブを分散させて成る導電性熱可塑性エラストマー組成物であって、(a)前記熱可塑性エラストマー材料のゴム分が樹脂系架橋剤により架橋されており、圧縮永久歪み(JIS K 6262法により70℃で22時間後の測定値をいう。以下、同様である)が30%以下であり、

(b)前記ゴムの配合量が前記熱可塑性エラストマー100重量部に対して225～400重量部の割合であり、(c)前記カーボンナノチューブは、直径が70nm以下であり、グラフェンシートを丸めた形状からなる平滑な面を有し、かつグラフェンシートからなる層が複数同心円状に配置されているものである、ことを特徴とする。

【0009】本発明の導電性熱可塑性エラストマー組成物は、圧縮永久歪み等の機械的特性に優れしかもリサイクル性を有することから、各種の電気部品や電子部品の導電材料として経済性よく利用することができる。

【0010】本発明の導電性熱可塑性エラストマー組成物は、次の実施態様を包含する。前記の本発明の導電性熱可塑性エラストマー組成物において、熱可塑性エラストマーとゴムとを混練した後、ゴムを動的架橋してなる熱可塑性エラストマー材料にカーボンナノチューブを分散させて成ることを特徴とする。前記の本発明の導電性熱可塑性エラストマー組成物において、前記動的架橋が押出機を用いて行われていることを特徴とする。

【0011】前記の本発明の導電性熱可塑性エラストマー組成物において、熱可塑性樹脂に予め分散させたカーボンナノチューブを、前記熱可塑性エラストマーに分散させることを特徴とする。前記の本発明の導電性熱可塑性エラストマー組成物において、カーボンナノチューブを熱可塑性エラストマーおよびゴムの合計量100重量部に対して1～30重量部を分散させてなることを特徴とする。

【0012】前記の本発明の導電性熱可塑性エラストマ

一組成物において、圧縮永久歪みが30%以下であることを特徴とする。

【0013】

【発明の実施の形態】本発明の導電性熱可塑性エラストマー組成物は、熱可塑性エラストマーとこれに配合した前記特定量のゴムとを必須の高分子材料として含み、この熱可塑性エラストマー材料を200℃付近の高温で混練しながらゴム分を架橋する薬品を添加して、ゴム分の架橋を進め、次いでカーボンナノチューブを分散することにより得られる。

【0014】本発明において材料の一つとなる熱可塑性エラストマーは、熱可塑性を有すること、すなわち熱により粘度が低下し柔らかくなり、冷却するとゴム弾性を有するものになる高分子材料であればよい。熱可塑性エラストマーとしては、とりわけスチレン-エチレン-ブチレン-スチレン樹脂、スチレン-エチレン-プロピレン-スチレン樹脂を用いるのが好ましく、さらにはエチレンの繰り返しユニットを主鎖に含むスチレン-エチレン-エチレン-プロピレン-スチレン(SEEPS)樹脂が強度も高く、もともとの圧縮永久歪みも小さいことからとりわけ好ましい。SEEPSの具体例としては、商品名「セプトン4077」、「セプトン4055」、「セプトン4033」(いずれも株式会社クラレ製)が挙げられる。これらのなかでも、GPCによる数平均分子量は30万程度と高い分子量を有している「セプトン4077」がとりわけ好ましく使用できる。

【0015】本発明においてもう一つの材料となるゴムはいずれのゴムでもよく、例えば天然ゴム、シス-1,4-ポリイソプレン、ハイシスポリブタジエン、スチレン-ブタジエン共重合体ゴム、エチレン-プロピレンゴム(EPDM)、エチレン-プロピレンジエンゴム(EPDM)、クロロプレンゴム、ブチルゴム、ハロゲン化ブチルゴム、アクリロニトリル-ブタジエン共重合体ゴムあるいはアクリルゴムなどが挙げられる。

【0016】これらの中でも、熱可塑性エラストマーとの親和性の面から、EPDMまたはEPDMが好ましく、架橋性を考慮するとEPDMが最も好ましく用いられる。EPDMとしては、各種のものが使用可能であり、エチレン含量の低いものは低温特性に優れ、エチレン含量の高いものは強度に優れる傾向がある。また、EPDMは、油展タイプでもよい。本発明において、前記のとおり、熱可塑性エラストマー100重量部に対してゴムは250～400重量部の割合で配合されるが、さらに好ましい割合は300～350重量部の範囲である。ゴム分が上記の範囲を超えると、後のゴムの架橋工程において、熱可塑性エラストマーの熱可塑性を維持することが困難になり、一方上記の範囲に達しないときは圧縮永久歪みが悪化する。なお、ゴムは前述のように油展タイプでもよいが、上記のゴム重量割合は油展されたオイルは含まれない。

【0017】熱可塑性エラストマーにゴムを配合した熱可塑性エラストマー材料の調製に際して、バッチ式混練機で調製するのは効率的ではなく、連続式の押出機を用いてゴム分を動的架橋しながら調製することが好ましい。この動的架橋には、樹脂系、過氧化物系の架橋剤のいずれでも架橋は一応可能であるが、実際に押出機による架橋には、架橋速度、臭気、物性等を考慮すると樹脂架橋が最も好ましい。硫黄架橋では非常に臭気は強く、加硫度も上がらない。過氧化物加硫は、押出機中での加硫が進みにくく、また反応進んでも制御が難しく発煙を

起こすことも有り得る。
【0018】樹脂架橋剤としては、アルキルフェノールホルムアルデヒド樹脂が好ましく、特に臭素を持つ反応型が好ましく、具体例としては商品名「タッキロール201」、「タッキロール250-I」あるいは「タッキロール250-III」（いずれも田岡化学製）などを挙げることができる。また、これらを適宜組合せて用いることにより架橋度の調整が可能である。架橋剤は、ゴム100重量部に対して5～20重量部、好ましくは10～15重量部の範囲である。また、樹脂加硫のためには、通常、酸化亜鉛を存在させることが必要であり、その量としてはゴム100重量部に対して1～10重量部、好ましくは2～5重量部の範囲である。

【0019】本発明においては、前記の可塑性エラストマーとゴムに加えて、他の樹脂材料を配合してもよく、例えばオレフィン樹脂とりわけポリプロピレンを配合することによって、導電性熱可塑性エラストマー組成物の外観を向上させかつ強度を大きくし、また耐傷つき性が改善される。ポリプロピレンはホモポリマーでもよいし、エチレンユニットを持ったブロックポリマー、またはエチレンとプロピレンのランダムコポリマーであってもよい。ポリプロピレンは、熱可塑性エラストマーとゴムとの合計量100重量部に対して5～40重量部の割合で配合することが好ましく、特に10～20重量部の範囲がより好ましい。

【0020】また、本発明の導電性熱可塑性エラストマーには、柔軟性の向上や加工性をよくするためにオイルを含有させておくことも可能であり、その量としては熱可塑性エラストマーとゴムの合計量100重量部に対して0～300重量部、好ましくは20～200重量部、さらに好ましくは50～150重量部である。更に、必要に応じて、酸化防止剤、光安定剤、紫外線吸収剤、顔料、充填剤あるいは加工助剤等を本発明の目的を阻害しない限りにおいて適量を添加してもよい。前記熱可塑性エラストマーとゴムは、ゴム架橋剤等の必要に応じて配合される添加物と共に2軸押出機を用いて200℃付近、スクリュウ回転数200rpm程度等の条件で押し出すことにより、前記熱可塑性エラストマー材料が調製される。この材料中では、微視的にみるとゴムが架橋されて小さな島となって、熱可塑性エラストマーと必要に

応じて配合されるポリプロピレンなどの樹脂のいわば海中に浮かんだ状態となっている。このようにして得られた熱可塑性エラストマー材料は、熱可塑性エラストマー単独の場合よりも、架橋したゴム分が存在するために圧縮永久歪みが小さくなって30%以下となり20%を切ることもある。また、射出成形や押出成形も可能である。

【0021】次に、上記の熱可塑性エラストマー材料中にカーボンナノチューブが分散される。カーボンナノチューブは、各種のタイプのものが知られており、径の程度にも大小がある。一般に、直径の小さいものほど表面積が大きく、導電性を付与する面で有利である。本発明においては、平均的な直径が15～30nmのものが好ましく、20nm以下であればさらに好ましく、また直径は実質的に一定であればより好ましい。更に、グラフェンシートを丸めた形状からなる平滑な側面を有し、かつグラフェンシートからなる層が複数同心円状に配置されているものであればよい。長さは、混練によっても切断されるので一概に範囲をきめることはむづかしいが、一般的に直径の100～1000倍程度のものを用いるがこの範囲に制限されるものではない。このような性能のカーボンナノチューブは既に市販されており、例えばハイビリオン・キャタリシス・インターナショナル社製のものを用いることができる。

【0022】本発明において、カーボンナノチューブは熱可塑性エラストマーおよびゴムの合計量100重量部に対して1～30重量部を分散させておくことが好ましく、この範囲のなかでも4～8重量部であれば一層好ましい。このような添加範囲であれば、導電性を付与でき、しかも得られる導電性熱可塑性エラストマーの加工性を実質的に低下させることはない。本発明でいう導電性とは、体積固有抵抗値を抵抗測定装置（例えば、アドバンテスト社製のもの）で測定したときに、安定に測定できる $10^7 \Omega \cdot \text{cm}$ 以下であることをいう。カーボンナノチューブは、そのまま上記の熱可塑性エラストマー材料に添加し分散してもよいし、予め熱可塑性エラストマーまたは他の熱可塑性樹脂に分散させたマスターバッチをブレンドすることも可能である。ここで、他の熱可塑性樹脂の種類は特に限定されるものではないが、熱可塑性エラストマーとの親和性がよい材料として例えば、ポリプロピレン、ポリスチレンあるいはポリエチレン等が好ましい。それ以外にも、ポリカーボネート、ポリアミド、ポリエステルあるいはポリウレタン等の熱可塑性樹脂を挙げることができる。

【0023】前記熱可塑性エラストマー材料とカーボンナノチューブ（またはそのマスターバッチ）を、再び例えば2軸押出機やバンバリー、ニーダー、小型混練機等で混練することにより、カーボンナノチューブを上記配合材料中に分散させることができる。これらの機種の中でも、連続的に製造することができる点において2軸押

出機の使用が有利である。カーボンナノチューブの分散状況によっては、2回もしくは3回以上繰り返して2軸押出機に投入して混練をより多く与えて分散をよくしてもよい。本発明の熱可塑性エラストマー組成物は、静電気の発生が少ない機械的特性に優れた高分子材料として各種の電気部品や電子部品の材料として用いることができる。例えば、OA機器のハウジング材や、導電性床材、中間転写ベルトの駆動ローラ等のOA部品などに使用することができる。

【0024】

【実施例】以下に、実施例および比較例を挙げて本発明をさらに具体的に説明する。

【0025】実施例1

熱可塑性エラストマーとしてSEEPS（商品名「セプトン4077」株式会社クラレ製）32重量部、ポリプロピレン11重量部、にパラフィンオイル57重量部を添加して、一晩置き、2軸1軸押出機（アイペックス社製）を用いて、180℃、200rpmで押し出してペレット化した。これに、酸化亜鉛3.5重量部、樹脂系架橋剤（商品名「タッキロール」201と「250-II」（田岡化学製）との3:1との混合物）12重量部、ポリプロピレン15重量部、ゴムとしてEPDM（商品名「エスプレン670F」、住友化学製）200重量部（オイル100重量部を含む）を加えて、同じ2軸1軸押出機に供給し、200℃、200rpmで動的架橋を行い、熱可塑性エラストマー材料を得た。上記で得た熱可塑性エラストマー材料を成形し、圧縮永久歪みを測定したところ13%であった。

【0026】次に、この熱可塑性エラストマー材料330.5重量部に、カーボンナノチューブのポリスチレンベースのマスターバッチ（カーボンナノチューブ重量分率20%、カーボンナノチューブ平均直径20nm；ハイペリオンキャタリシスインターナショナル社製）40重量部を添加して、2軸押出機（神戸製鋼社製）で200℃、200rpmで混練して、本発明の導電性熱可塑性エラストマー組成物を得た。

【0027】本熱可塑性エラストマー組成物の導電性を抵抗測定装置（アドバンテスト社製）で測定したところ、体積固有抵抗値が測定限界以下（ $10^7 \Omega \cdot \text{cm}$ ）であった。この導電性熱可塑性エラストマー組成物をモンサントプロセサビリティータスターにより200℃で押し出すと細いストランドが得られたことから、熱可塑性であることを確認できた。また、この導電性熱可塑性エラストマー組成物を成形して圧縮永久歪みを測定したところ25%であり、十分に優れた値を示した。さらに、この導電性熱可塑性エラストマー組成物を1軸の押出機でチューブ状に押し出したところ、非常にきれいな外観のチューブが得られた。

【0028】実施例2

実施例1においてカーボンナノチューブのポリスチレン

ベースのマスターバッチを20重量部としたこと以外は、実施例1と同様に調製して本発明の導電性熱可塑性エラストマーを得た。また体積固有抵抗を測定したところ $10^{11} \Omega \cdot \text{cm}$ であった。

【0029】実施例3

熱可塑性エラストマーとしてSEEPS（商品名「セプト4077」株式会社クラレ製）32重量部、ポリプロピレン11重量部、にパラフィンオイル57重量部を添加して、一晩置き、2軸1軸押出機（アイペックス社製）を用いて180℃、200rpmで押し出してペレット化した。これに酸化亜鉛3.5重量部、樹脂系架橋剤9重量部、ポリプロピレン15重量部、ゴムとしてEPDM（商品名「エスプレン670F」、住友化学製）144重量部（オイル72重量部を含む）を加えて、同じ2軸1軸押出機に供給し、200℃、200rpmで動的架橋を行い、熱可塑性エラストマー材料を得た。

【0030】次に、この熱可塑性エラストマー材料271.5重量部に、カーボンナノチューブのポリスチレンベースのマスターバッチ（カーボンナノチューブ重量分率20%、カーボンナノチューブ平均直径20nm；ハイペリオンキャタリシスインターナショナル社製）40重量部を添加して、2軸押出機（神戸製鋼社製）で200℃、200rpmで混練して、本発明の導電性熱可塑性エラストマー組成物を得た。この体積固有抵抗は測定限界以下であった。

【0031】実施例4

樹脂系架橋剤16重量部、ゴムとしてEPDM（商品名「エスプレン670F」、住友化学製）256重量部（オイル128重量部を含む）を加えて動的架橋したこと以外は実施例3と同様にして熱可塑性エラストマーを得た。この熱可塑性エラストマー材料390.5重量部にカーボンナノチューブのポリスチレンベースのマスターバッチ40重量部を添加して、2軸押出機で混練した以外は実施例3と同様にして導電性熱可塑性エラストマー組成物を得た。この体積固有抵抗は $10^7 \cdot \text{cm}$ であった。

【0032】比較例1

実施例1においてカーボンナノチューブのポリエチレンベースのマスターバッチを無添加としたこと以外は、実施例1と同様に調製して熱可塑性エラストマーを得た。このものを成形して永久圧縮歪みを測定したところ13%であった。また体積固有抵抗を測定したところ $10^{16} \Omega \cdot \text{cm}$ であった。

【0033】比較例2

実施例1においてカーボンナノチューブのポリエチレンベースのマスターバッチを5重量部としたこと以外は、実施例1と同様に調製して熱可塑性エラストマーを得た。このものを成形して永久圧縮歪みを測定したところ17%であったが、体積固有抵抗値は $10^{16} \Omega \cdot \text{cm}$ であった。

【0034】比較例3

実施例1において調製した熱可塑性エラストマーに、カーボンナノチューブに代えて、ケッチェンブラックEC25重量部を、2軸押出機を用いて添加した。この調製物の体積固有抵抗は測定限界以下であったが、圧縮永久歪みを測定したところ38%であり高過ぎるものであった。また、1軸押出機でゆっくりとチューブを押し出したところ、温度が上がりすぎ、荒れた外観のチューブしか得られなかった。

【0035】比較例4

熱可塑性エラストマーとしてSEEPS（商品名「セプトン4077」、クラレ株式会社製）32重量部、ポリプロピレン11重量部、にパラフィンオイル57重量部を添加して、一晩置き、2軸1軸押出機（アイスペック社製）を用いて、180℃、200rpmで押し出してペレット化した。これにカーボンナノチューブのポリエチレンベースのマスターバッチ（カーボンナノチューブ重量分率20%、カーボンナノチューブ平均直径20nm；ハイペリオンキャタリシスインターナショナル社製）20重量部を添加して、2軸押出機（神戸製鋼社製）で200℃、200rpmで混練して成形した。この調製物の圧縮永久歪みを測定したところ38%と高過ぎるものであった。なお、体積固有抵抗は測定限界以下

であった。

【0036】

【発明の効果】本発明の熱可塑性エラストマー組成物は、何度でも射出成形が可能（すなわちリサイクル使用が可能）であり、例えば工程内廃材でも無駄なく使用できることから製造コストが低減される。本発明において、カーボンナノチューブを分散する前に調製される熱可塑性エラストマー材料は、熱可塑性エラストマーと共に架橋されたゴム分を含んでいるために、通常熱可塑性エラストマーとは比較にならないほどの低い圧縮永久歪みを有する。すなわち、圧縮永久歪みは、通常熱可塑性エラストマーが通常40%以上であるのに対して、本発明のカーボンナノチューブを分散した熱可塑性エラストマー組成物は、圧縮永久歪みが30%以下であり、またデュロメータA硬度は50前後であり非常に柔軟であることから、電気部品や電子部品へ利用するにあたってきわめてよい機械的特性を有する。

【0037】また、本発明によると、カーボンナノチューブの添加量は、従来の導電性付与物質例えば通常カーボンブラック等と比較して、非常に少量でも導電性を付与できることから、得られる導電性熱可塑性エラストマー組成物は流動性に優れ、押出成形、射出成形した際にも非常にきれいな外観の製品が得られる。

フロントページの続き

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